

Catalysts for the control of coking during steam reforming

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Abstract

Catalytic steam reforming of light hydrocarbons is the major industrial route to the production of hydrogen and synthesis gas. The product spectrum is dictated by thermodynamics, with hydrogen favoured at high temperatures. The formation of coke, also favoured under these conditions, is a major problem.

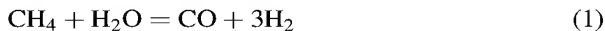
The mechanism of coke formation is reviewed and different approaches to control coking are discussed. Ensemble size control produced by adsorbing controlled amounts of sulphur on the nickel surface has been found to be very effective at controlling coking. An approach based on the prevention of carbide formation has also been shown to be extremely effective, although the exact mechanism of coke minimisation is uncertain. Small amounts of tin reduce coking very significantly.

Indications exist that the use of rare earth oxides as supports can also reduce coking. Further study of this finding is recommended. © 1999 Elsevier Science B.V. All rights reserved.

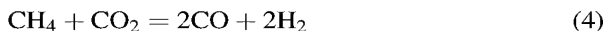
Keywords: Coking; Synthesis gas; Steam reforming

1. Introduction

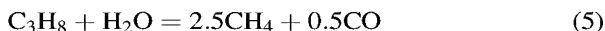
The steam reforming of methane and light hydrocarbons is the major industrial process for the manufacture of synthesis gas and hydrogen [1,2]



In some cases, carbon dioxide may replace steam to give a more favourable H_2 :CO ratio for subsequent reactions of the products [3].

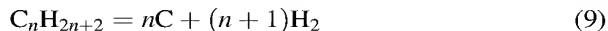


The product spectra from all these reactions is controlled predominantly by thermodynamics. Methane is the favoured product at lower temperatures



with hydrogen being preferred at temperatures in excess of ca. 700–800°C [1,2]. Depending on the application, the hydrogen containing product gas leaves the reformer at temperatures between 700°C and 950°C (4).

The necessity to operate at these temperatures introduces several potential problems. The thermal stability of the catalyst is certainly one [5], with steam tending to favour catalyst and support sintering [6]. However, the major problem lies in the formation of coke.



These reactions are in equilibrium and the formation of coke via reactions (7) and (8) becomes less

favoured as the temperature increases [1,2]. However, coke formation via reactions (6) and (9) becomes increasingly important at higher temperatures and depending on the nature of the feed (7), can rapidly deactivate the catalyst and block the reactor.

Minimisation of coking is one of the major factors controlling the industrial application of steam reforming [1,2]. The thermodynamics of the process dictate that reaction conditions that favour coke formation cannot be avoided, but operating conditions can be chosen to minimise coke. Perhaps the most obvious way is to increase the steam to hydrocarbon or the carbon dioxide:hydrocarbon ratios in order to favour the reverse of reactions (7) and (8). Rostrup-Nielsen et al. [4] have presented carbon limit diagrams which relate the propensity of the catalyst to coke to the H:C and O:C ratios in the gas phase.

The success of such measures is easily seen from the wide industrial application of steam reforming. Nonetheless, the provision of high temperature steam is expensive, and any measures to reduce coke formation have a significant economic advantage for the process. As a result, the formation and removal of coke continues to be a subject of considerable interest.

The approaches to the problem rest on an understanding of the mechanism of coke formation. As a result, it is useful first to describe the various ways in which coke can be formed.

2. Coking during steam reforming

Although steam reforming is a catalysed reaction, the operating conditions are such that homogeneous gas phase reactions are also possible. Thus “coke” is a collective description of various kinds of carbonaceous deposit formed in the reactor. Rostrup-Nielsen has identified pyrolytic carbon, encapsulating coke and whisker coke present in a tubular steam reformer [7]. Pyrolytic coke originates from thermal cracking of hydrocarbons above ca. 600°C (for methane) which encapsulates the catalyst and the reactor internals. The origins of encapsulating and whisker coke are catalytic and are described in more detail below.

Pyrolytic coke originates from a free radical process which produces tars, polymers and coke [8]. At least some of the deposit is formed by condensation of a high molecular weight material on any cool surface –

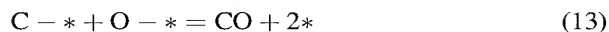
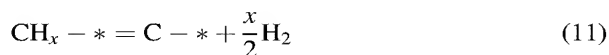
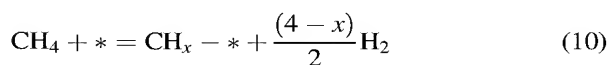
from the catalyst to the heat exchanger. Since the reaction to form these intermediates is in the gas phase, minimisation of heated space and dilution of the free radical concentration (in order to avoid polymerisation) helps to minimise coke formation. Where the diluent is steam, gasification of coke and intermediates leading to coke is possible, although the reactions have been shown to be fairly slow [9].

Coke formation promoted by a catalyst is more complex and is harder to minimise. It is important to remember that coke accumulation is a more accurate description, in that it is the balance between formation and removal of coke which dictates catalyst coking.

Industrial steam reforming catalysts are normally based on nickel [1,2]. Cobalt and the noble metals are active catalysts but are more expensive. Despite the fact that carbon formation is significantly less likely over noble metals [1], the economic advantages of the use of nickel still favour the use of this metal.

Thermal stability of the catalysts is important, particularly since the Tammann temperature, above which nickel sintering can be expected (590°C), is less than the normal operating temperatures (ca. 800–900°C) for steam reforming [5]. The use of a support not only induces thermal stability but also offers an opportunity for assistance with coke control.

There is a general agreement that steam reforming proceeds via the dissociative adsorption of hydrocarbons on the catalyst surface. For methane, the reaction may be written as



The dissociative adsorption of methane has been found to be structure sensitive, with the activation energy on Ni(1 1 0) and Ni(1 1 1) being higher than on Ni(1 0 0) [10]. Reasonable agreement was found between the rate of methane decomposition and the overall rate of steam reforming, inferring that reaction (10) is rate determining. Further reaction of carbonaceous intermediates to coke is possible, but coke accumulation is slow.

The dissociative adsorption of higher hydrocarbons on nickel is much faster than that of methane [1,7], but a similar sequence of reactions can be used to describe steam reforming [1,2,4]. Since the formation of carbonaceous intermediates is faster, the rate of carbon accumulation on the surface would also be expected to be faster and coking should be more pronounced. This is found to be the case in practise.

Coke formation on nickel surfaces is fairly well understood, although not all aspects of the process are completely clear. It is believed that hydrocarbons dissociate to produce highly reactive monatomic carbon (C_α) [11,12]. C_α is easily gasified by reactions such as reaction (13) above to form carbon monoxide. However, if there is an excess of C_α formed or gasification is slow, then polymerisation to C_β is favoured. Tests have shown that C_β is much less reactive than C_α [9], and gasification is much slower. As a result, C_β may accumulate on the surface or may dissolve in the nickel.

Dissolution of carbon in nickel is essential to the growth of carbon whiskers [13,14]. The process begins apparently by the formation of nickel carbide [13,14], although this is not certain since the carbide is not stable under conditions where the sample can be analysed. However, traces of nickel carbide have been observed, and iron carbide is known to be an important intermediate in a similar coking process on iron [15].

Once the carbon has dissolved/formed a compound with nickel, diffusion through the metal particle to a grain boundary occurs. There is some dispute whether this is temperature driven or driven by a concentration difference involving preferred precipitation at a dislocation [12–14]. The net result is, however, that carbon precipitates out and lifts the nickel particle at the tip of a growing whisker. The nickel remains as an active catalyst, but the accumulation of carbon whiskers blocks the catalyst bed and increases pressure drop to unacceptable levels.

Gasification of carbon whiskers occurs via the reverse process, with carbon diffusing through the nickel particle to be gasified on the catalytic surface [9].

Not all of the coke formed on the surface dissolves in nickel. At least some carbon remains on the surface and encapsulates nickel [13,14]. It is uncertain whether the encapsulants involve only C_β or also includes polymers originating partially in the gas

phase. Deposits formed on the surface can contain fairly ordered structures, possibly formed via dehydrogenation, surface migration and growth. Once formed, however, the encapsulants deactivate the catalyst and are considerably harder to gasify than, for example, C_α .

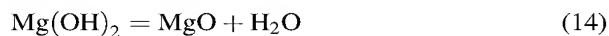
Overall, then, coke formation on nickel results from a balance between coke formation and gasification. Catalyst deactivation may result from encapsulation, with whisker coke not affecting greatly the activity of the catalyst but causing reactor blockage and pressure drop.

Steam reforming involves not only nickel. The support has a major role to play in providing thermal stability and in assisting coke removal. It is well known [16] that basic catalysts promote the reaction between steam and carbon, and catalyst supports are chosen with this in mind. ICI favour the use of potassium hydroxide, Haldor Topsoe favour magnesia and British Gas have used urania [17]. In all cases, precautions have to be taken to maintain the stability of the catalyst.

Although potassium hydroxide favours coke gasification, it can also reduce catalytic activity [18]. This has been suggested to result from the enhancement of structural reorganisation by the alkali [19], the less active Ni(1 1 1) face being preferred. However, there is no proof of the suggestion.

Perhaps of more importance is the tendency for potassium hydroxide to volatilise in steam at high temperatures [2]. ICI solved this problem by the use of complex potassium alumina–silicate and calcium magnesia silicate. The potassium is liberated slowly as the involatile K_2CO_3 which is hydrolysed to the hydroxide. Mobility on the surface ensures good coke–alkali contact and rapid gasification [2].

Haldor Topsoe favour a more important role for magnesia in the support, with magnesium spinels offering good thermal stability. It is necessary to heat up the system with care, since the hydrolysis equilibrium



favours hydration at temperatures below about 425°C [1,2]. The formation of hydroxide results in a decrease in the structural strength of the catalyst. As a result, steam is not introduced to the system on start-up until the temperature exceeds ca. 450°C.

Overall, it is clear that coke formation and gasification occurs in the gas phase and on the catalytic metal. Coke removal can be assisted by the support. In both cases an excess of steam is required.

3. Coke minimisation

Various approaches to coke minimisation can be explained in terms of the mechanism of coke formation described above.

The first approach rests on the concept of *ensemble size control* [19]. It is clear from reactions (10)–(13), that steam reforming requires the dissociative adsorption of a hydrocarbon to form a carbonaceous intermediate. It is also clear that coke formation, at least on the catalyst, originates from this same carbonaceous intermediate (reactions (6)–(9)). How, then, to control the selectivity of the reaction to favour steam reforming rather than coke formation?

Rostrup-Nielsen [19] argued that coke formation would require an ensemble of surface sites that would be larger than that required for steam reforming. The formation of carbon – either dissolved in or deposited on the nickel – must require the polymerisation of monatomic carbon species (C_α), while gasification involves only one such species. Given the course of dissociative adsorption (reactions (10) and (11)), the formation of more than one C_α species demands more surface sites. As a result, it was reasoned that, by controlling the number of sites in an ensemble, it may be possible to minimise coking whilst maintaining steam reforming.

The basis of the ensemble size control was found in the work of Alstrup and Andersen [20] on sulphur adsorption on nickel. They found that the surface grid of sulphur did not coincide with the surface grid of the metal atoms. In fact, sulphur occupies a fourfold hollow site on Ni(1 0 0), independent of coverage at low pressures. At higher coverages, the sulphur occupies a (2×2) structure, probably best described as a nickel sulphide surface containing islands of free nickel sites [21].

Adsorption of sulphur on the surface thus delineates ensembles of sites, with the critical size being found to exist at sulphur coverages in excess of 0.7–0.8. Under these conditions, the rate of steam reforming was reduced but coke formation was essentially elimi-

nated. Some amorphous carbon was deposited, and a new form of whisker carbon (christened octopus carbon) could be produced under extreme conditions.

Adsorption of sulphur on nickel, although strong, is a dynamic process [19]. As a result, it is necessary to add small quantities of a sulphur producing gas to the feed. For hydrogen sulphide, an H_2S/H_2 ratio greater than 7.5×10^{-7} was found to be sufficient to maintain the ensemble size control. Too large a supply of hydrogen sulphide led, as expected, to total deactivation of the catalyst.

The ensemble size control approach has proved to be very useful, being developed into an industrial process (SPARG process) [19]. Very careful control of the sulphur levels in the feed is essential to “minimal coke” operation.

The second approach to control of coke formation is based on the idea of *preventing carbide formation* [22]. Carbide was suggested to be the essential intermediate en route to coke. It was reasoned that prevention of carbide formation on the surface could slow down the whole process of coke formation, since dissolution and precipitation could probably only occur via carbide formation.

The electronic structure of carbon is very similar to the electronic structure of the tetra- and penta-valent p metals (such as Ge, Sn and Pb or As, Sb or Bi) and of sulphur. These elements contain “spare” p electrons in their outer shell close to a stable s-orbital. With carbon, nickel carbide is formed from the interaction of 2p electrons from the carbon with the 3d electrons of the nickel. Thus it would seem possible that tetra- or penta-valent p metals could also interact with Ni 3d electrons, thereby reducing the chance of nickel carbide formation [23].

Formation of an alloy to reduce carbide formation may be a possibility, but it is undesirable to lose the overall properties of nickel, since steam reforming must be catalysed. However, carbide formation can only be expected at the surface and as a result, an alloy which is formed only at the surface should be preferred. This means, in effect, that the second component should be expected to surface segregate [24,25]. Focusing on possible dopants, the probability of surface segregation was calculated using data originating from Miedema [27] and theory developed by Jeng et al. [28], in which equilibrium surface segregation is driven mainly by the lowering of surface energy and

Table 1
The effect of dopants on Ni catalysts

Dopant	%	Expected surface segregation	Expected cluster formation	Expected formation of		Significant effect on	
				Alloys	Surface compounds	Steam reforming ^a	Coke formation ^b
Pt	1	—	—	+		—	—
Ir	1	—	—	+		—	—
Sn	1	+	+		+	—	+
Pb	1	+	+		+	+	+
Ge	1	+	+		+	—	—
As	1	+	+			+	+
Sb	1	+	+			—	+
Bi	1	+	+		+	—	+
Ag	1	+	+	+	+	+	+
Cu	2	+	—	+		—	—
Zn	1	+	+		+	—	+

^aForty mg catalyst+2060 mg α -alumina; total flow=290 ml mm⁻¹; CH₄=27%, H₂O=8%, H₂=32%, He=33%, T=600°C.

^bMeasured using a microbalance: Total flow 290 ml mm⁻¹; CH₄=61%, H₂O=7%, H₂=20%, N₂=12%, T=500–800°C.

the relief of bulk strain energy. The probability of surface segregation calculated by this method is shown in Table 1. No great differences were observed when other methods of assessing surface segregation were used [23–26].

Steam reforming and carbon formation were assessed over these doped catalysts (see below). Those that showed promise were examined using X-ray photoelectron spectroscopy [29]. The results confirmed surface segregation of the dopants.

Although surface segregation may occur, formation of an alloy with the dopant does not necessarily follow. The possible formation of alloys or of surface compounds was calculated using the method described by Miedema et al. [24,25]. Where possible the predictions were compared with the information available in phase diagrams [30] and showed good agreement. Results are summarised in Table 1.

It must be emphasised that the above arguments are based on the non-proven importance of nickel carbide in the system. It could be that surface enrichment by a dopant is forming clusters, which define an ensemble. In order to check this, calculations of the importance of clustering were carried out, using the criteria developed by Somorjai [26]. The results, shown in Table 1 show that non-transition metals are more likely to form clusters and as a result to delineate ensembles.

The effect of small amounts of dopants on catalytic and coking performance of the supported nickel was then compared with predictions based on the ideas

summarised above (Table 1). It is clear that dopants that surface segregate have a significant effect on the overall process and with the exception of Ag, dopants that are expected to form surface compounds also influence the process. However, cluster formation (which may indicate ensemble size control) is expected in many of the catalysts in which the dopant has a significant effect. What is clear, however, is that the dopant can decrease coke formation while having little effect on steam reforming. As a result, some of the catalysts were tested in more detail.

It is known that coke formation varies with temperature, and steam reforming and coke formation were explored over a range of temperature. Typical results are shown in Fig. 1. The effect of tin on steam reforming was small until more than 1.75% was added. Coke formation on the other hand, was significantly reduced even by the addition of 0.5% Sn. Thus, it is clear that addition of small amounts of dopant does significantly reduce coking while having little effect on steam reforming.

The one remaining possibility for minimisation of coke accumulation is to accelerate coke gasification. Iridium is thought to play such a role in catalytic reforming [31], and as a result, the efficiency of all catalysts for coke gasification was tested. None of the systems listed in Table 1 showed enhanced gasification of coke compared to supported nickel. Even in the presence of iridium, coke gasification by steam was only 70% of the rate measured over pure nickel [23].

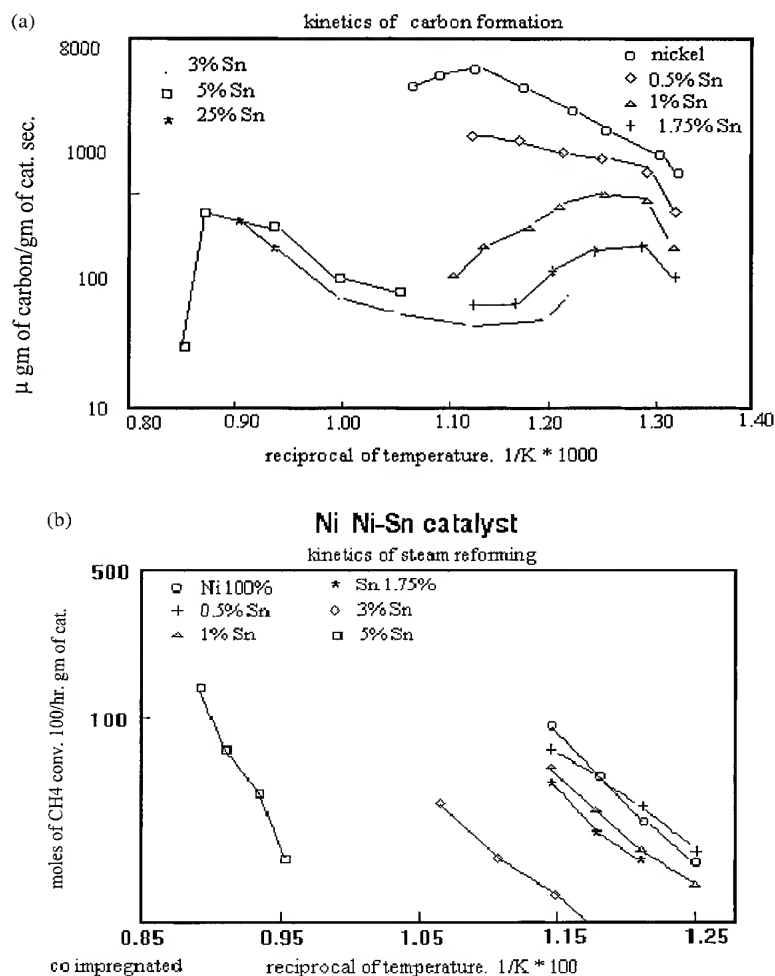


Fig. 1. (a) Steam reforming and coke formation over supported nickel catalysts doped with various amounts of tin; (b) 40 mg catalyst+2060 mg α -alumina; total flow=290 ml mm^{-1} ; CH_4 =27%, H_2O =8%, H_2 =32%, He =33%, T =600°C.

It is clear that the reasoning used to develop catalysts that favour steam reforming with minimal coke formation is far from proven. Indeed, it is uncertain whether the dopants act by prevention of carbide formation or by delineating ensembles on the surface (see Table 1). What is clear, is that catalysts can be doped to minimise coking, and that industrial operation of the system is feasible [32].

Some measure of the overall performance of catalysts doped with various metals can be obtained by comparing the efficiency of steam reforming with that of coke formation (Table 2). It is seen that although

the presence of a second metal reduces methane conversion, many of the metal dopants increase the amount of carbon oxides produced (reflecting the rate of steam reforming) and decrease the amount of coke. Balancing methane conversion against selectivity for steam reforming over coke formation, catalyst containing tin are seen to be optional. These have been developed for industrial use [32].

Minimisation of coking is also a function of the support, and here attention has been focused recently on the role of rare earth oxides [33]. Horiuchi et al. [34] have reported that basic metal oxides affect both

Table 2
Steam reforming and coking on doped catalysts

Catalyst (metal component)	Total methane ^a converted	Amount of CO _x ^a produced	Coke formation ^a	Steam reforming rate, Coke formation rate
100% Ni	0.765	0.408	0.358	1.14
75% Ni, 25% Pb	0.51	0.103	0.2	3.98
0.5% Sn, 99.5% Ni	0.53	0.425	0.21	4.05
1.75% Sn, 98.25% Ni	0.288	0.263	0.025	10.5
1% Sb, 99% Ni	0.47	0.3675	0.103	3.59
0.5% As, 99.5% Ni	0.24	0.21	0.028	7.64
0.5% Ag, 99.5% Ni	0.298	0.263	0.035	7.5

^aValues given in g mol h⁻¹ g⁻¹ catalyst. Total flow=290 ml min⁻¹; CH₄=27%, H₂O=8%, H₂=32%, He=33%. Coke by difference T=600°C.

carbon dioxide reforming and carbon formation, but there is more interest in the effect of the rare earths. The oxides appear slightly to enhance steam reforming, and significantly to decrease coke formation by increasing coke gasification. Ceria itself, is inactive for steam reforming but combinations of nickel and ceria gave a much improved coking performance [35]. At least part of the effect was due to increased adsorption of water on the ceria support and to increased carbon gasification [33,35,36]. Although certainly showing much promise, the role of rare earth oxides in steam reforming catalysis needs to be explored in greater depth.

Catalyst deactivation – either by coke formation or by thermal sintering – is a fact of life with steam reforming catalysts. It is clear, however, that understanding the process of deactivation can lead to optimised catalysts in which these problems are minimised. Nonetheless, this is not the complete answer, in that different fuels have been found to give very different coking rates [7]. It has been found to be possible to steam reform feed stocks which contain significant amounts of, for example, aromatics, but this is far from easy. At some stage, it is necessary to turn from steam reforming to partial oxidation to produce hydrogen [37]. The extent of coking, even over an optimised catalyst, is an important factor in the choice of process.

4. Conclusions

The mechanism of coke formation during steam reforming has been explored and used to explain various methods of coke control.

Ensemble size control on the surface of nickel via the addition of controlled amounts of sulphur have been found to reduce coking.

The addition of metals expected to interact with nickel to prevent the formation of nickel carbide have been found to reduce coking. Novel catalysts containing small amounts of tin have promise as industrial catalysts that promote steam reforming with minimal formation of coke.

Rare earth oxides added to the support appear to favour coke gasification. Further study of their importance is recommended.

Acknowledgements

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